



Review

Recent advances in the selective catalytic reduction of NO_x with NH₃ on Cu-Chabazite catalystsJihui Wang^a, Huawang Zhao^a, Gary Haller^b, Yongdan Li^{a,b,*}^a Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China^b Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, New Haven, CT 06511, USA

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ABSTRACT

The development of Cu-chabazite (CHA) catalysts, i.e. Cu-SSZ-13 and Cu-SAPO-34, represents a significant technology breakthrough for the removal of NO_x by selective catalytic reduction (SCR) with ammonia. Cu-CHA catalysts show an excellent hydrothermal stability towards high temperature aging and wide active temperature windows for the ammonia SCR reaction. This work summarizes the recent progress in the development of the Cu-CHA catalysts for the NH₃-SCR reaction. The state of Cu in the reaction and the preparation methods on the catalytic performance are discussed. The advances in the understanding of the reaction mechanism are reviewed. The hydrothermal stability of the typical Cu-CHA catalysts are compared.

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Contents

1. Introduction	346
2. State of Cu in the catalyst	347
3. Catalyst preparation	348
3.1. The effect of preparation condition	348
3.2. One-pot synthesis of Cu-CHA catalyst	349
4. Reaction mechanism and kinetics	350
5. Hydrothermal stability	353
6. Conclusions and perspectives	353
Appendix A. Supplementary data	354
References	354

1. Introduction

Nitrogen oxides (NO_x), in the flue gas of industrial combustion and vehicle exhaust, are among the major air pollutants that lead to a number of environmental problems such as photochemical smog, acid rain and haze. To meet the stringent emission

standards, many approaches, such as three-way catalysis [1], NO_x storage and reduction (NSR) and selective catalytic reduction (SCR) of NO_x with ammonia, to reduce the NO_x emissions have been intensively explored. Among these techniques, the SCR of NO_x with NH₃ is considered to be the most efficient technology for reducing NO_x emission in the presence of excess oxygen [2]. V₂O₅-WO₃(MoO₃)/TiO₂ material has been commercially employed as a NH₃-SCR catalyst for a number of years. However, several serious problems with this catalyst still remain, e.g. the narrow temperature window, i.e. only applicable in 300–400 °C, the high activity of SO₂ oxidation, and the toxicity of V₂O₅ [3]. Therefore, new catalysts with environmentally benign characteristics and high SCR performance in a wide temperature range are required. Since the

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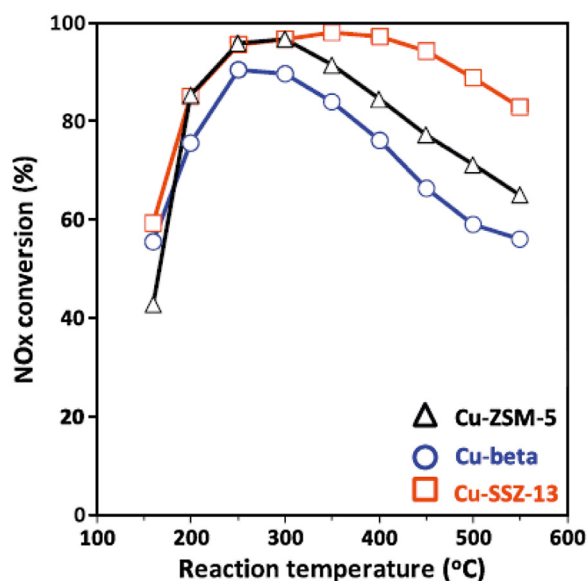


Fig. 1. NO_x conversion profiles for Cu-SSZ-13, Cu-beta and Cu-ZSM-5 at various temperatures. Reaction conditions: 350 ppm NO, 350 ppm NH₃, 14% O₂ and 2% H₂O with a balance of N₂.

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discovery of Cu-ZSM-5 catalyst as an efficient catalyst for NO_x removal in 1986 by Iwamoto *et al.* [4], Cu-exchanged zeolites such as ZSM-5, BEA and Y have been investigated [5]. However, the poor hydrothermal stability of Cu-exchanged of those zeolite catalysts significantly limits their application in the treatment of exhaust gas from diesel engine [5].

Recently, Cu-SAPO-34 [6] and Cu-SSZ-13 [7] (Chabazite structured) catalysts with very high hydrothermal stability and activity for the NH₃-SCR reaction under oxidizing conditions were discovered by the industrial researchers. Kwak *et al.* [8] first reported the performance of Cu-SSZ-13 in NH₃-SCR reaction, with comparison to the data of Cu-BEA and Cu-ZSM-5 zeolites. The order of the catalyst performance observed was Cu-SSZ-13 > Cu-ZSM-5 > Cu-Beta (see Fig. 1), that is the inverse order of the pore size. SAPO-34 and SSZ-13 are typical examples of zeolites with the CHA structure, that have small pore radius of eight-membered rings (3.8 Å). Both Cu-SSZ-13 and Cu-SAPO-34 samples are reported to maintain their high SCR performance even after hydrothermal aging at 800 °C [9]. Although SAPO-34 and SSZ-13 share the same CHA structure, Cu-SAPO-34 is more complicated than Cu-SSZ-13 [10–13]. Unlike SSZ-13, in which Brønsted acid sites are highly dependent on the content of Al, the Brønsted acid sites of SAPO-34 are attributed to the introduction of Si atoms into the neutral AlPO₄-34 framework [14]. It was proposed that Si atoms incorporate into the AlPO₄-34 structure by two different substitution mechanisms: the first one (denoted as SM1) is that the Si substitution for phosphorus form Si(4Al) entities, which give rise to negative charges for forming Brønsted acid sites; the second mechanism (denoted as SM2) is the double substitution of neighboring aluminum and phosphorus by two silicon atoms to form Si(nAl) (n = 3–6) structures, which leads to the formation of stronger Brønsted acid sites [12,14]. However, a large amount of Si islands are formed when Si content is high, which has no acid site. Many factors including the template, the Al and Si source, the molar ratio of Si/Al/P/template of the gel, the reaction temperature and reaction time influence the dispersion of Si in the SAPO-34 [14–16]. This makes it difficult to determine the acid density and acid strength of SAPO-34.

Recently, the advances in the removal of NO_x by NH₃-SCR reaction over CHA-based catalysts are reviewed by Beale *et al.* [17] and Moliner *et al.* [18]. They mainly discussed the key findings of the

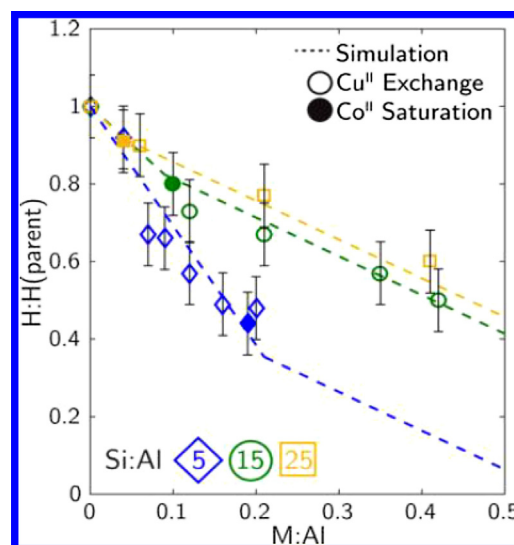


Fig. 2. Residual H⁺ sites per parent sample H⁺ from NH₃ titrations on oxidized M-SSZ-13 samples versus extent of M/Al exchange for Si:Al = 5 (blue \diamond), 15 (green \circ), and 25 (orange \square). Open and filled symbols denote Cu²⁺ and saturated Co²⁺ exchange, respectively. Dashed lines are model predictions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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synthesis method and characterization work over CHA-structured based zeolite catalysts. In this work, we pay attention to the state of Cu in the reaction over Cu-CHA catalysts. The reaction mechanism, and the comparison between Cu-SSZ-13 and Cu-SAPO-34 catalysts as well as the future prospects, are outlined.

2. State of Cu in the catalyst

The performance of the Cu-CHA catalyst strongly depends on the chemical state of Cu during the reaction. It is now accepted that the isolated Cu²⁺ is the active sites in Cu-CHA catalyst for NH₃-SCR reaction [19–21]. Gao *et al.* [22] investigated the influence of the ion-exchange level on the Cu species in Cu-SSZ-13 catalyst. They found that the catalysts with low-exchange level contain exclusively isolated Cu²⁺ at the 6-membered ring sites containing two framework Al atoms. Due to the high SCR activity of the samples, the isolated Cu²⁺ at the 6-membered ring sites of SSZ-13 is believed to be the active site for the SCR reaction. However, with the further increase of the ion-exchange level, a Cu₂O_y species (clustered Cu²⁺ ions, y ≥ 1) forms and locates at the 8-membered ring. This species also is found to be active for ammonia oxidation. Verma *et al.* [23] also evaluated the Cu species in Cu-SSZ-13 catalysts with Si/Al atomic ratio of 4.5 and found that there is a theoretical limit for the density (Cu:Al atomic ratio = 0.2) of the isolated Cu²⁺ at the 6-membered rings in SSZ-13. Beyond this limit, a part of the isolated Cu²⁺ ions convert to Cu dimers. Based on the operando characterization and density functional theory (DFT) calculations [19,20], the isolated Cu²⁺ at the 6-membered ring sites of SSZ-13 was confirmed to be the active site for the NH₃-SCR reaction under realistic conditions at low temperatures. The NH₃-SCR reaction was proposed to be associated with a closed redox cycle between Cu²⁺ and Cu⁺/H⁺ formed at the 6-membered rings containing two framework Al atoms [20].

The isolated Cu²⁺ was found to firstly occupy the site in 6-membered ring with 2 Al atoms after dehydration [24–26], when the similar sites saturate, the Cu species may exist with an OH extra-ligand coordinate to the 1 Al sites. Paolucci *et al.* [27] confirmed this result by the experiments and DFT simulation. As shown in Fig. 2, at

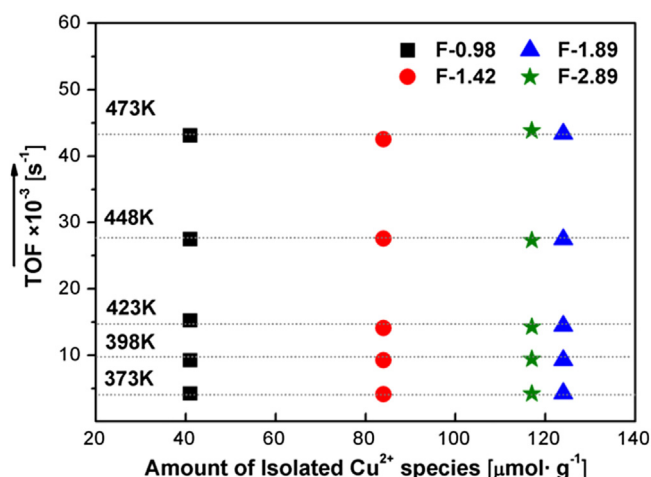


Fig. 3. Turnover frequency (TOF) calculated based on the amount of isolated Cu^{2+} ions in the Cu/SAPO-34 catalysts with different Cu loading. Conditions: 500 ppm NO, 500 ppm NH_3 , 5% O_2 balanced with N_2 , 100–200 °C. Reprinted from [31] with permission of Elsevier Science Publishers B.V.

a Si:Al ratio of 5, each exchanged Cu cation decreased the number of residual H^+ sites by a factor of two (on average) up to a Cu:Al ratio of 0.20. For the samples with Si:Al ratios of 15 and 25, each exchanged Cu exchanged two H^+ sites up to Cu:Al ratios of 0.10 and 0.04. It is consistent to the number of 2 Al sites in the 6-membered rings from DFT simulation. Furthermore, this is identified by the Co^{2+} exchange experiment, because Co^{2+} does not exchange at single Al sites as $[\text{Co}^{2+}\text{OH}]^+$ at the exchanging pH used in the work (pH \approx 3.2). This indicates that the 2 Al sites in 6-membered rings are the preferred sites for the exchanged Cu^{2+} , these sites are saturated before remaining 1 Al sites are populated with $[\text{CuOH}]^+$.

In contrast to the Cu-SSZ-13 catalyst in which Cu is only present as isolated Cu^{2+} ions, CuOx clearly coexist with the isolated Cu^{2+} ions in the Cu-SAPO-34 catalyst even with very low Cu loading [15]. In the low-temperature range (<200 °C), CuOx species is found to make no contribution and the SCR reaction mainly occurred on the isolated Cu^{2+} sites [15]. Dong *et al.* [28], found that a high content of isolated Cu^{2+} sites favors NOx removal activity of Cu-SAPO-34 catalyst at low-temperature range but inhibits it in the high-temperature. The incorporation of Ce^{3+} to Cu-SSZ-13 catalyst through ion-exchange method enhances the aging resistance of the catalysts [29]. The existence of Ce^{3+} inhibits the conversion of the active isolated Cu^{2+} sites to Cu^+ during the hydrothermal aging process. Yu *et al.* [30] examined the state of Cu in a Cu-SAPO-34 catalyst during the NH_3 -SCR reaction with an *in-situ* electron paramagnetic resonance (EPR) technique. They found that the isolated Cu^{2+} species is reduced to Cu^+ when the catalyst is exposed to NH_3 feed at 270 °C. The following NOx purge leads to the consumption of the adsorbed NH_3 and the recovery of isolated Cu^{2+} . These results clearly indicate that the isolated Cu^{2+} ions is the active site of the Cu-SAPO-34 catalyst for NH_3 -SCR reaction. Xue *et al.* [31] came to a similar conclusion in their kinetics study. They found that the turnover frequency (TOF) calculated based on the amount of isolated Cu^{2+} ions on the samples with different Cu loading is a constant value at the same temperature (Fig. 3).

3. Catalyst preparation

3.1. The effect of preparation condition

The technique for the incorporation of Cu into the CHA zeolite is a key factor in the preparation of the Cu-CHA catalyst. Normally, most preparations of Cu-CHA catalyst adopt a wet ion-exchange

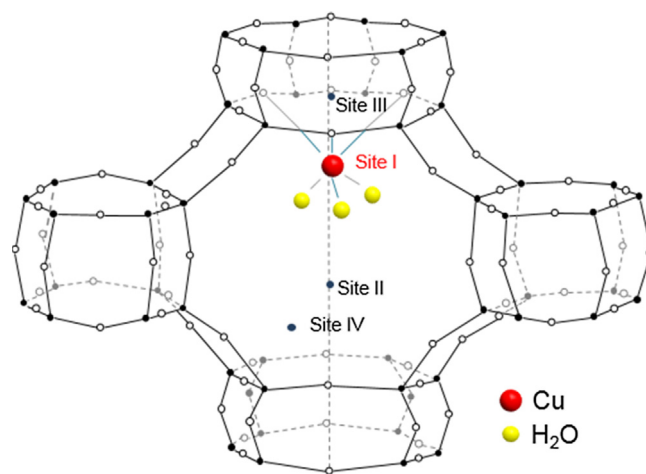


Fig. 4. The diagram of the unit cell of CHA structure. Reprinted from [31] with permission of Elsevier Science Publishers B.V.

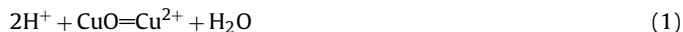
method which involves the synthesis of CHA zeolites and the subsequent wet ion-exchange with copper salt solution. This method allows more Cu^{2+} ions to be located at the exchange sites of the CHA zeolites. However, other techniques such as chemical vapor deposition [32], solid state ion-exchange (SSIE) [33,34], “one-pot” with Cu ions introduced by structural directing agent [34,35], wet mixing [11] and impregnation techniques [11] have also been examined for the preparation of Cu-CHA catalysts.

As shown in Table 1, the catalysts prepared with different methods have different Cu species and therefore exhibit different catalytic performance and hydrothermal stability. Deka *et al.* [32] prepared Cu-SSZ-13 catalysts with conventional wet ion-exchange and chemical vapor deposition methods. The activity test results indicated that the catalyst prepared by a conventional wet ion-exchange method shows much higher NO conversion and N_2 selectivity than other catalyst samples. They found that the isolated Cu^{2+} ions at the 6-membered ring sites of SSZ-13 dominate the catalyst prepared with the wet ion-exchange method, while both isolated Cu^{2+} ions and CuAlO_2 -type species coexist in the catalyst sample prepared with the chemical vapor deposition method. For the sample prepared with chemical vapor deposition, the lack of isolated Cu^{2+} ions leads to low catalytic activity, and the presence of CuAlO_2 favors N_2O formation and thus decreases the N_2 selectivity. The ion-exchange seems a good method to prepare the Cu-SSZ-13 with good activity. In contrast to the ion-exchanged Cu-SSZ-13 in which copper is predominately present as isolated Cu^{2+} ions even at rather high ion-exchange levels [15]. For the SAPO-34, it is difficult to get a Cu-SAPO-34 with only isolated Cu^{2+} in this method [15,34,36]. Gao *et al.* [15] found that even dilute copper acetate solution (0.01 M), very moderate temperatures (50 °C), and short contact time (1 h) were applied during ion-exchange, CuOx clearly coexist with the isolated Cu^{2+} ions in the Cu-SAPO-34 catalysts even with very low Cu loading. More seriously, during solution ion-exchange SAPO-34 undergoes different extent of structural damage via irreversible hydrolysis. The solid state ion-exchange, one-pot synthesis techniques and impregnation may be better ways to prepare Cu-SAPO-34. The impregnation method is also a common way to introduce the active metal. However large amount of CuO form in the Cu-SAPO-34 which enhances the NH_3 oxidation at high temperatures [36,37]. The addition of a second metal ion may suppress the formation of CuO phase. Cao *et al.* [37] report that introduction of additives effectively improves the dispersion of copper species, increases the amount of isolated copper ions. In the solid state ion exchange method, heating up a CuO and SAPO-34 mixture to an

Table 1
Influence of the preparation method on the Cu species in Cu-CHA catalyst.

References	Catalyst	Preparation method	Main Cu species	Analysis technique
Deka et al. [32]	Cu-SSZ-13	Wet ion-exchange	Isolated Cu ²⁺	XANES
Deka et al. [32]	Cu-SSZ-13	Chemical vapor deposition	Isolated Cu ²⁺ and CuAlO ₂	XANES
Wang et al. [33]	Cu-SSZ-13	Solid state ion-exchange	Isolated Cu ²⁺ and CuO	DRIFTS and XRD
Xie et al. [35]	Cu-SSZ-13	One-Pot	Isolated Cu ²⁺ and CuO	H ₂ -TPR
Gao et al. [34]	Cu-SAPO-34	Solid state ion-exchange	Isolated Cu ²⁺ and CuO	H ₂ -TPR and XRD
Gao et al. [34]	Cu-SAPO-34	One-Pot	Isolated Cu ²⁺ and CuO	H ₂ -TPR and XRD
Yan et al. [11]	Cu-SAPO-34	Wet ion-exchange	Isolated Cu ²⁺ in the ellipsoidal cavity	H ₂ -TPR and EPR
Yan et al. [11]	Cu-SAPO-34	Wet mixing	Isolated Cu ²⁺ near the eight-ring window, Cu _x O _y	H ₂ -TPR and EPR
Yan et al. [11]	Cu-SAPO-34	Impregnation	Isolated Cu ²⁺ near the right-ring window, Cu _x O _y	H ₂ -TPR and EPR

elevated temperature (700 °C and above) allows for the formation of extra-framework Cu²⁺ according to the following reactions:



This method makes the control of Cu loading facile. However, incomplete CuO reaction and partial damage of the zeolites at such high temperature are the drawbacks [33,34,38]. Recently, Shwan *et al.* [39] found that NH₃ and/or a standard NH₃-SCR feed allow solid state ion exchange at lower temperatures (250 °C).

For the Cu-CHA catalysts prepared with solid state ion-exchange [33,34] and one-pot synthesis [34,35] techniques, CuO was found to coexist with the isolated Cu²⁺ ions. CuO makes no contribution to the SCR activity in the low-temperature range, and decreases the performance in the high temperature range as a result of NH₃ over-oxidation [22,35].

There exist four cationic sites in the CHA framework (Fig. 4, [31]). Site I is located at the 6-membered rings in the ellipsoidal cavity. Site II is placed near the center of the ellipsoidal cavity. Site III is in the center of the hexagonal prism face. Site IV attaches to the 8-membered ring window [40]. Different preparation methods also result in the different location of the isolated Cu²⁺ ions in CHA zeolite framework, and influence the hydrothermal stability of the catalysts. Yan *et al.* [11] prepared Cu-SAPO-34 catalysts with three different methods, i.e. conventional wet ion-exchange, wet mixing and impregnation methods. After aging at 800 °C for 50 h in a flowing gas containing 10% of H₂O in air, the catalyst prepared through wet ion-exchange method shows much higher activity than the other two samples. They found that the isolated Cu²⁺ species is in the ellipsoidal cavity (site I) for the ion-exchange sample, while this species locates near the eight-ring window (site IV) in the wet-mixing and impregnation samples. Due to the steric hindrance, Cu²⁺ ions at site I are more active and stable than those at site IV [16].

Generally, compared to the conventional wet ion-exchange samples, the Cu-CHA catalysts prepared from the other methods show lower activity and hydrothermal stability. However, due to the complexity of the preparation procedure of wet ion-exchange, the one-pot synthesis method becomes meaningful.

3.2. One-pot synthesis of Cu-CHA catalyst

The application of SSZ-13 zeolite in SCR catalyst is limited due to the high cost of the template N,N,N-trimethyl-1-adamantammonium hydroxide (TMAda). In order to lower the cost, the one-pot synthesis approach in which the Cu ions are introduced by a structural directing agent was developed. Ren *et al.* [41] first reported a one-pot method with a copper complex made from CuSO₄·5H₂O and tetraethylenepentamine (molar ratio of 1/1, Cu-TEPA for short) as template. The obtained material exhibits typical peaks of SSZ-13 zeolite in XRD pattern and excellent SCR activity. However, the Cu loading of their one-pot sample was as high as 9.5–10.2 wt%, much higher than that (2.8 wt%, 100% exchange level) of the Cu-SSZ-13 prepared by the wet ion-exchange method

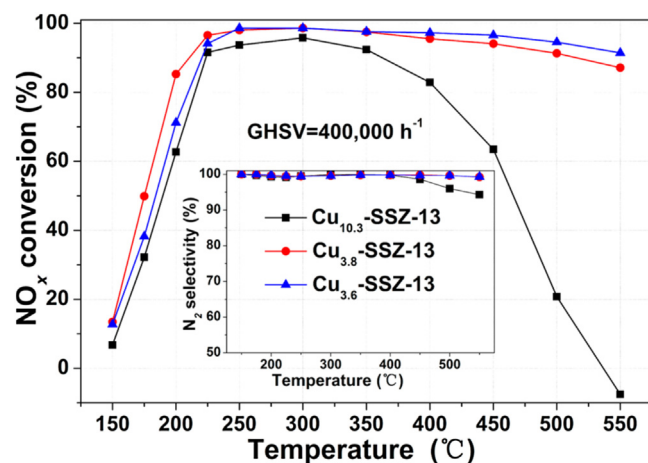


Fig. 5. NO_x conversion and N₂ selectivity over Cu_x-SSZ-13 catalysts prepared with a one-pot method with different Cu loading. x represents the Cu content in the catalyst by weight.

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[42]. In general, the Cu-CHA catalysts show lower hydrothermal stability in high temperature aging with an increase of the Cu content, due to the formation of the CuO_x species that accelerates the collapse of the zeolite framework [43]. Further study indicates that the Cu loading of one-pot Cu-SSZ-13 catalyst can be lowered by an ion-exchange with a NH₄NO₃ solution [35]. The lower Cu loading leads to a higher NO_x conversion (shown in Fig. 5). Guo *et al.* [44] found that the ion exchange process with NH₄NO₃ for the one-pot Cu-SSZ-13 catalyst not only removes a part of Cu ions, but also allows the remaining Cu ions to relocate from the large cages to the 6-membered ring sites, which enhances the SCR activity and the hydrothermal stability of the catalyst. It is noted that the Cu loading of the Cu-SSZ-13 catalyst prepared with the one-pot synthesis method should be minimized in order to improve the high-temperature hydrothermal stability.

It is well known that SAPO-34 zeolite is sensitive to water vapor at low-temperatures, and that crystallinity loss occurs due to the hydrolysis of the framework [15]. Leistner and Olsson [45] investigated the deactivation of Cu-SAPO-34 catalyst during low-temperature aging. The samples were aged at 70 °C under the flow of N₂ containing 400 ppm NH₃, 400 ppm NO, 8% O₂ and 5% H₂O. The activity of the aged catalysts was much lower than that of the fresh ones. They tried to regenerate the deactivated catalyst under high temperature with dry gas flow, but failed. As with the high-temperature hydrothermal stability, the stability of SCR catalyst at low-temperature is also important, because during the start-up period the temperature of the exhaust gas is low. Wang *et al.* [46] prepared a number of Cu-SAPO-34 catalysts with different Cu loadings by the one-pot synthesis method. They treated the catalysts hydrothermally with 80% humidity at 70 °C and found that the increase of the Cu loading enhances the hydrothermal stability

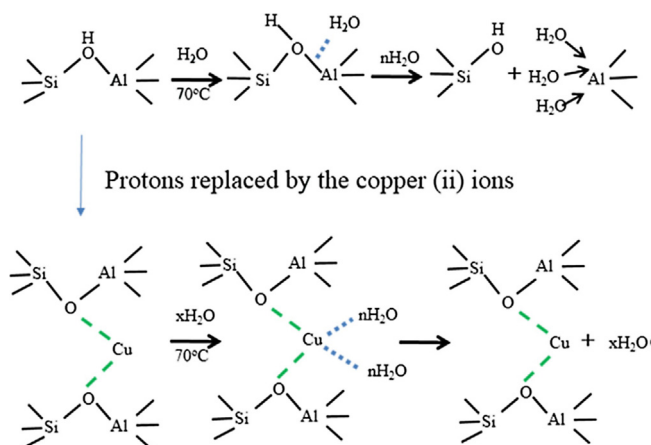


Fig. 6. The scheme of SAPO-34 deactivation by water vapor at low-temperature range and the protection of Cu²⁺ on SAPO-34.

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of the Cu-SAPO-34 catalyst. The presence of more Cu ions protects the Si-O-Al bonds by shielding them from H₂O molecules. They proposed a mechanism as shown in Fig. 6. As the high Cu loading has a detrimental effect on the high-temperature hydrothermal stability of the catalyst [47], the Cu loading of the Cu-SAPO-34 catalysts prepared by one-pot synthesis method should be optimized to balance the hydrothermal stability both at low-temperature and high-temperature ranges.

In order to improve the performance of Cu-CHA catalyst prepared with the one-pot method, much attention has been paid to the selection of the template. Martínez-Franco *et al.* [48] employed a mixture of Cu-TEPA and TMAda as the template in the synthesis of a Cu-SSZ-13 catalyst. The sample they obtained shows higher hydrothermal stability for aging at 750 °C than the one prepared with only Cu-TEPA as the template. In another work of the same group [49], a mixture of tetraethylammonium cation (TEA) and Cu-TEPA were applied as the template in the synthesis of a Cu-SAPO-34 catalyst. They showed that TEA molecules compete with the Cu-TEPA complex during the nucleation and crystallization process of SAPO-34, which reduces the Cu loading amount and facilitates a high solid yield. Compared to the Cu-SAPO-34 catalyst prepared with Cu-TEPA as the only template, the existence of the co-template TEA also leads to more isolated Si atoms in the zeolite framework. The appropriate distribution of the negative charges, or the isolated Si⁴⁺ atoms, stabilize the extra-framework Cu²⁺ ions and enhance the hydrothermal stability of the Cu-SAPO-34 catalyst.

It is important to note that after hydrothermal aging at 750 °C, the SCR performance of the Cu-CHA catalyst prepared by one-pot method are lower than those prepared via the conventional wet ion-exchange route [9,48,49].

4. Reaction mechanism and kinetics

It is often discussed that the NH₃-SCR reaction occurs on the catalyst surface via two mechanisms: (1) Eley-Rideal mechanism, NH₃ is first adsorbed onto Lewis or Brønsted acid sites, then the adsorbed NH₃ species react with gaseous or weakly adsorbed NO_x to produce N₂ and H₂O; (2) Langmuir-Hinshelwood mechanism, the adsorbed NH₃ species reacts with chemisorbed NO_x species to accomplish the SCR reaction [2,3]. Su *et al.* [50] investigated the reaction mechanism of SCR reaction over a Cu-SSZ-13 catalyst with the in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and temperature programmed surface reaction (TPSR) techniques. They proposed the reaction mechanism as given in Fig. 7, in which the SCR reaction mainly happens via the reac-

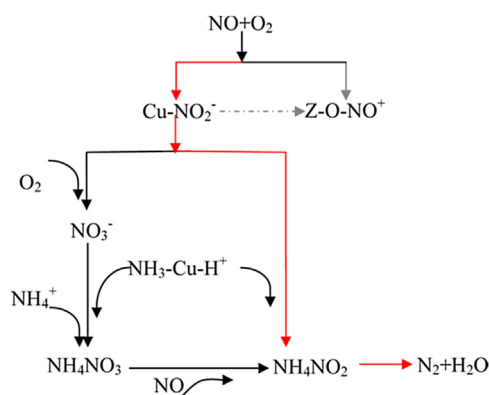


Fig. 7. The scheme of the SCR reaction pathways over Cu-SSZ-13 catalyst at low temperatures.

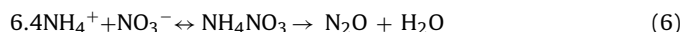
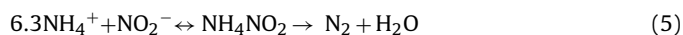
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tion as the first step between NH₃ adsorbed on Lewis acid site and the directly formed NO₂⁻. These adsorbed species react and form ammonia nitrite (NH₄NO₂) which further decomposes into N₂ and H₂O. They suggest that nitrate (NO₃⁻) is difficult to form due to the high reactivity of NO₂⁻, which was consumed by the adsorbed NH₃ before it could be further oxidized to NO₃⁻. Furthermore, the in-situ DRIFTS results suggest that the NH₃ adsorbed on the Lewis acid site is more active than that on the Brønsted acid site. Lezcano-Gonzalez *et al.* [51] also found that NH₃ linked to the Cu²⁺ Lewis sites was indispensable for the NH₃-SCR reaction over a Cu-SSZ-13 catalyst, while Brønsted centers act primarily as NH₃ storage sites. Gao *et al.* [25] found that the addition of Li⁺ and Na⁺ to the Cu-SSZ-13 catalysts enhances the hydrothermal stability of the catalysts. The introduction of cocations removes a part of zeolitic Brønsted acid sites that are most vulnerable to hydrolysis during hydrothermal aging. This result also proves a secondary role of Brønsted acid sites in the Cu-CHA catalysts for the NH₃-SCR reaction.

Crandell *et al.* [52] employed DRIFTS and DFT calculation techniques and investigated the reaction intermediates during NH₃-SCR reaction over a Cu-SSZ-13 catalyst. A NO⁺ species was supposed to be the key intermediate during the reaction. Moreover, the NO⁺ species further reacts with chemisorbed oxygen to form NO₂⁻ as shown in Eq. (1) [30].



For the reaction mechanism of NH₃-SCR over the Cu-SAPO-34 catalyst, Yu *et al.* [30] observed that the formation of N₂O is closely related with the existence of NH₄NO₃, while NH₄NO₂ species decomposes easily to N₂ and H₂O. The reaction mechanism can be described as follows:



Yu *et al.* [30] also found that the NH₃ adsorbed on Lewis acid sites is preferentially consumed during the NH₃-SCR reaction, then the NH₄⁺ species linked to the Brønsted acid site migrates to the Lewis acid sites and participates in the reaction. This phenomenon is similar to that observed over a Cu-SSZ-13 catalyst [50,51]. Wang *et al.* [53] examined the reaction pathways of the NH₃-SCR reaction over a Cu-SAPO-34 catalyst at low temperatures, and proposed that, as shown in Fig. 8, in addition to the decomposition of NH₄NO₂,

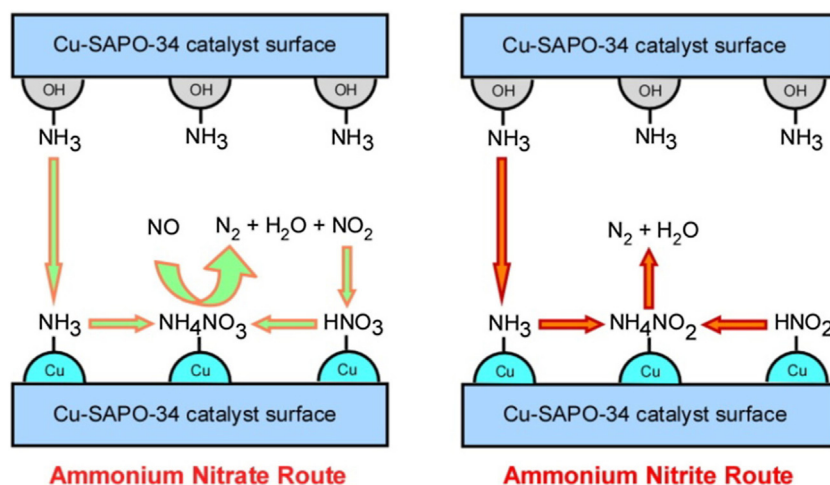


Fig. 8. The scheme of SCR reaction mechanism over the Cu-SAPO-34 catalyst at low temperatures. Reprinted from [53] with permission of American Chemical Society.

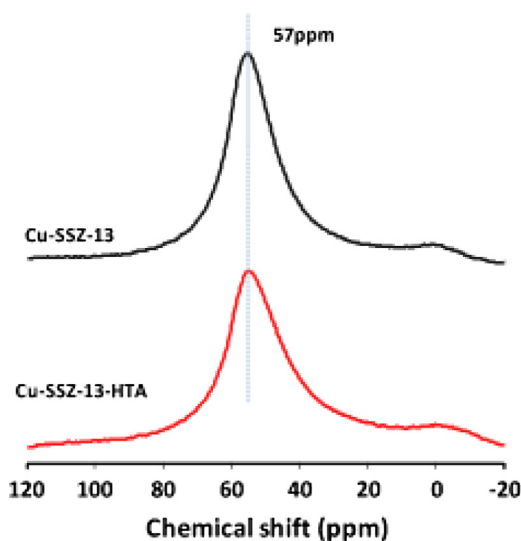


Fig. 9. Solid state ²⁷Al-NMR spectra of Cu/SSZ-13 before and after hydrothermal aging. Reprinted from [58] with permission of Elsevier Science Publishers B.V.

the SCR reaction also involves the formation of NH₄NO₃ and its subsequent reduction with NO as:



The NH₄NO₃ can be reduced by NO at a temperature as low as 100 °C, which contributes to the excellent low-temperature activity of the catalyst. The different opinions on the roles of NH₄NO₃ in NH₃-SCR reaction of Yu *et al.* [30] and Wang *et al.* [53] may arise from the different reaction temperatures examined by them, viz. 100 °C for Yu and 290 °C for Wang. These results indicate that the NH₃-SCR reaction pathway over the Cu-SAPO-34 catalyst may change with the change of the reaction temperature. The reduction of the intermediate NH₄NO₃ with NO dominates the low-temperature SCR performance. However, NH₄NO₃ also decomposes to N₂O at low temperatures. The decomposition of NH₄NO₂ is the main pathway for NH₃-SCR reaction at high temperatures.

The apparent activation energies of the Cu-CHA catalysts in NH₃-SCR reaction are summarized in Table 2 [24,31,54,55]. Gao *et al.* [24] investigated the kinetics of Cu-SSZ-13 catalyst in NH₃-SCR reaction and found that the apparent activation energy for the catalysts with low Cu loadings is around 40 kJ/mol. In another work of the same group [14], the structure-activity relationships

Table 2
Apparent activation energy of Cu-CHA catalysts in NH₃-SCR reaction.

References	Catalyst	Temperature	Activation Energy (E _a), kJ/mol
Gao <i>et al.</i> [24]	Cu-SSZ-13	110–200 °C	40
Kwak <i>et al.</i> [54]	Cu-SSZ-13	150–250 °C	41
Xue <i>et al.</i> [31]	Cu-SAPO-34	100–200 °C	34
Fan <i>et al.</i> [55]	Cu-SAPO-34	125–225 °C	32

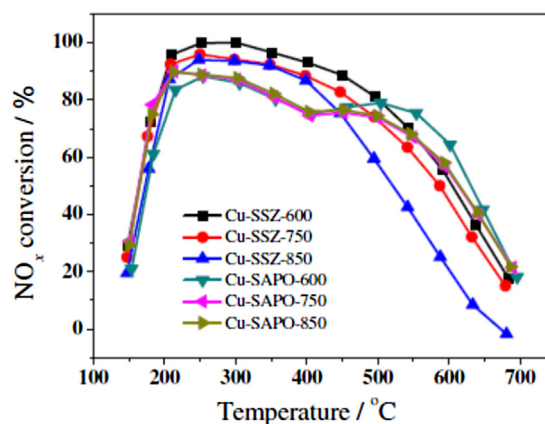


Fig. 10. NO_x conversions of Cu-SSZ-13 and Cu-SAPO-34 catalysts after hydrothermal aging at different temperatures. Reprinted from [9] with permission of Elsevier Science Publishers B.V.

of the Cu-SSZ-13 catalyst in NH₃-SCR reaction were explored. The results indicate that the SCR reaction rate over the Cu-SSZ-13 catalyst is a few times lower than those on the Cu-ZSM-5 and Cu-BEA catalysts. They found that the intra-particle diffusion limitation cannot be excluded, which is attributed to the fact that the SCR reactant molecules have kinetic diameters very close to the openings of the CHA structure. Leistner *et al.* [56] found the formation of NH₄NO₃ species over Cu-CHA catalysts during the SCR reaction, that resulted in the blockage of the small pores and the lowering of the reaction rates more than Cu-BEA catalyst. As exhibited in Table 2, the Cu-SAPO-34 catalysts have lower apparent activation energies for the NH₃-SCR reaction than those of the Cu-SSZ catalysts. This phenomenon may be ascribed to the more severe intra-particle diffusion limitation of the Cu-SAPO-34 catalysts [22].

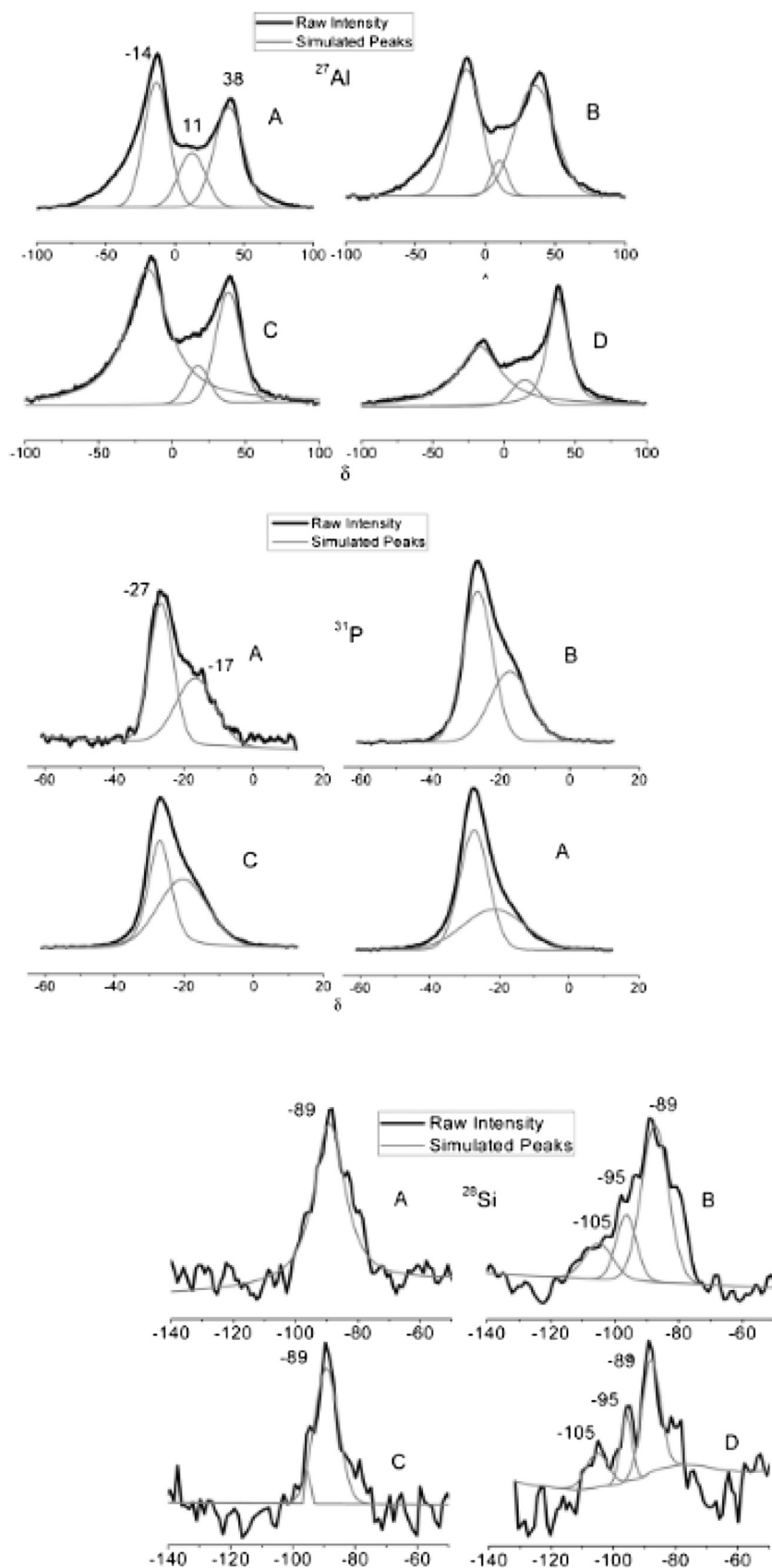


Fig. 11. MAS NMR spectra of ^{27}Al , ^{31}P and ^{28}Si for fresh and aged (at 800°C) H/SAPO-34 and 2 wt% Cu/SAPO-34 catalysts. The spectra of fresh H/SAPO-34; B spectra of aged H/SAPO-34; C spectra of fresh Cu/SAPO-34; D spectra of aged Cu/SAPO-34. Reprinted from [63] with permission of Royal Society of Chemistry.

5. Hydrothermal stability

Cu-SSZ-13 and Cu-SAPO-34 are recognized as commercially promising SCR catalysts due to their excellent hydrothermal stability. Fickel *et al.* [57] found that both Cu-SSZ-13 and Cu-SAPO-34 display superior SCR performance after treated at 750 °C for 15 h. Kwak *et al.* [58] compared the hydrothermal stability with Cu-ZSM-5 and Cu-beta. After hydrothermal aging at 800 °C for 16 h, the NO_x reduction performance of Cu-ZSM-5 and Cu-beta was significantly reduced, while that of Cu-SSZ-13 was not affected. Fickel *et al.* [59] proposed that the detached Al(OH)₃, cannot exit in the pores of the framework and Al may even reattach back to the framework during the hydrothermal aging process, arising from its relatively large kinetic diameter. However the dealumination is still the main reason for the collapse of the zeolite. As shown in Fig. 9, less reduction in the intensity of the tetrahedral aluminum peak was observed for Cu-SSZ-13 than both Cu-ZSM-5 and Cu-beta. The extent of delamination is readily probed with solid-state ²⁷Al NMR. However, the detached Al cannot be detected, probably due to the presence of paramagnetic Cu species react with Al to Cu-Al-like species. Vennestrom *et al.* [60] and Gao *et al.* [34] found the Cu-Al-like species exists as CuAl₂O₄ based on the results of EXAFS and EPR, respectively.

However, for Cu-CHA catalysts, Cu-SAPO-34 was found to be more robust than the Cu-SSZ-13 catalyst towards severe hydrothermal aging tests [38]. Ma *et al.* [9] compared the hydrothermal stability of a Cu-SSZ-13 and a Cu-SAPO-34 catalyst. As shown in Fig. 10, the good performance of both the two catalysts maintained upon aging at 750 °C for 16 h in simulated exhaust gases containing water. However, a significant difference between the two samples appeared after hydrothermal aging at 850 °C. Cu-SAPO-34 catalyst still maintained its high performance with even a slight increase of NO_x conversion in low-temperature range, while a remarkable activity loss was observed with the Cu-SSZ-13 sample. Wang *et al.* [38] observed a similar phenomenon, that is, hydrothermal aging at 800 °C results in a significant drop of NO_x conversion for a Cu-SSZ-13 catalyst but a slight enhancement of the performance for a Cu-SAPO-34 catalyst. XRD results showed that the CHA framework collapses for the Cu-SSZ-13 catalyst after hydrothermal aging, but it still remains for the Cu-SAPO-34 sample upon the same aging process. Moreover, they proposed that the enhancement of NO_x conversion for Cu-SAPO-34 after high temperature treatment may be attributed to a post solid state ion exchange process driven by the high temperature, increasing the number of active sites.

The migration of Cu species in Cu-SAPO-34 catalyst during high temperature aging was observed [61,62]. Upon aging, the Cu species outside the crystal migrate to the ion-exchangeable sites of the SAPO-34 lattice, enhancing the SCR performance as a result. However, no such ionic migration was observed with the Cu-SSZ-13 sample [58]. Wang *et al.* [16] evaluated the influence of the hydrothermal aging of a Cu-SAPO-34 catalyst at 750 °C on catalytic performance. Compared to the fresh catalyst, the aged sample shows a higher NO_x conversion in the temperature range 125–600 °C. H₂-TPR results demonstrate that the aged catalyst has a higher Cu²⁺ (site I)/Cu²⁺ (site III) ratio, suggesting the movement of the Cu²⁺ ions to more stable and active sites driven by the high-temperature treatment [16].

A healing process, *i.e.* the migration of phosphorus atoms to framework vacancies, caused by desilication, transformation to P(OAl)₄ species may be the reason for the high stability of SAPO-34 [12]. Fig. 11 shows the ²⁷Al, ³¹P and ²⁸Si NMR spectra for fresh and aged (at 800 °C) H/SAPO-34 and 2 wt% Cu/SAPO-34 catalysts [63]. Harsh hydrothermal treatment caused a decrease in the proportion of non-framework Al and P atoms and an increase in the proportion of framework Al and P atoms. The ratio of Si(4Al) species decreased and the ratio of both Si(3Al) and Si(2Al) species increased, indicat-

ing the migration of non-framework Al and P atoms to the defects induced by desilication [63]. Although the desilication leading to the formation of siliceous islands and aggregates, it restrains the structure of Cu-SAPO-34. Furthermore, Petitto *et al.* [64] found that the high content of silicon in the Cu-SAPO-34 leads to more Si island is harmful to the stability of catalyst due to the more severe desilication process.

Generally, Cu-SAPO-34 shows higher hydrothermal stability than Cu-SSZ-13 catalyst under severe aging conditions. The migration of Cu ions driven by high temperature contributes to the high stability of the Cu-SAPO-34 catalysts. The difference of the hydrothermal stability of Cu-SAPO-34 and Cu-SSZ-13 catalyst may arise from the different structure and charge density of the two zeolite frameworks [15,25,65]. In order to enhance the stability of the catalysts in the high temperature treatment. The appropriate Si/Al ratio for SSZ-13 and Si/(Si + Al + P) is necessary [16,66]. The low Cu content is essential to the hydrothermal stability due to the agglomeration of isolated Cu²⁺ destroys the structure of the catalyst [10,38]. The excess of Brønsted acid site is the most vulnerable for the H₂O attack [15,25,67]. The introduction of co-cation to reduce the Brønsted acid site seems to be a good choice to enhance the hydrothermal stability of Cu-CHA catalyst [25,29,67]. Gao *et al.* [25] found that the ion-exchange of Na into the Cu-SSZ-13 enhances both the activity and hydrothermal stability of the catalyst. The reduction of Brønsted acid sites is the main reason for the improvement of the catalyst performance. The suitable content of the co-cation is significant for the catalysts to stand a good activity and stability.

6. Conclusions and perspectives

The development of the Cu-CHA catalysts represents a major breakthrough in the area of NH₃-SCR. The published results indicate that Cu-CHA catalysts show much better hydrothermal stability than the other Cu-based zeolite catalysts, which is crucial for the application of these catalysts in the treatment of exhaust gas from diesel engines. In addition to the conventional wet ion-exchange method, several other technologies have also been employed to prepare the Cu-CHA catalysts. Due to the low cost and simplicity, the one-pot synthesis route is a promising technology for the preparation of the Cu-CHA catalysts.

The reaction mechanism of NH₃-SCR reaction over the Cu-CHA catalysts were examined. Langmuir-Hinshelwood mechanism with the formation of NH₄NO₂ and NH₄NO₃ intermediates was proposed. However, whether the presence of Eley-Rideal mechanism operates or has not been demonstrated. Furthermore, the SCR reaction was found to be controlled by the intra-particle diffusion due to the small openings of the CHA structures.

Cu-SAPO-34 appears to be more robust than the Cu-SSZ-13 catalysts under severe hydrothermal aging, although the reverse is true at low temperature. The migration of Cu species and plays a key role in the high hydrothermal stability of the Cu-SAPO-34 sample. For the practical use of Cu-CHA in NH₃-SCR reaction, several challenges remain:

- 1 Cu-SAPO-34 is sensitive to moisture at low temperatures. A better understanding and reduction of moisture sensitivity of Cu-SAPO-34 is a high priority.
- 2 Cu-CHA catalysts prepared by the one-pot method show lower hydrothermal stability than those from conventional wet ion-exchange technique. In order to improve the hydrothermal stability, more work should be performed to control the composition and structure evolution in the one-pot preparation process.

- 3 The hydrothermal stability of Cu-CHA catalysts should be further enhanced. More attention should be paid to appropriate Si/Al ratio, relatively low Cu content and Brønsted acid sites as well as suitable co-cations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.09.024>.

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